

栗柄金粉蕨的黄酮类成分*

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摘要: 从栗柄金粉蕨 (*Onychium lucidum*) 地上部分的甲醇抽提物中分到 10 个成分, 经详细的一维、二维核磁数据分析, 它们被鉴定为: 木犀草甙 (1), 3, 7-二甲基槲皮素 (2), 高山甙 B (3), 金粉蕨素 (4), 栗柄醇 (5), 金粉蕨醇 B (6), β -谷甾醇 (7), 胡萝卜甙 (8), 齐墩果酸 (9) 和蔗糖 (10)。栗柄醇系新成分。1, 2, 9 系首次由金粉蕨属分到。

关键词: 中国蕨科; 栗柄金粉蕨; 黄酮; 黄酮甙; 甲氧基环多醇。

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Flavonoids of *Onychium lucidum*

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Abstract: Ten compounds were isolated from the methanolic extract of the aerial parts of *Onychium lucidum*. These compounds were identified as luteoloside (1), 3, 7-dimethylquercetin (2), contigoside B (3), onychin (4), lucidol (1β -methoxy- 2β , 3α , 4β , 5α , 6β -pentahydroxycyclohexane) (5), onychiol B (6), β -sitosterol (7), daucosterol (8), oleanolic acid (9) and sucrose (10). Compound 5 is a new constituent, while 1, 2 and 9 were isolated from the genus *Onychium* for the first time. Their structures were elucidated on the basis of detailed spectroscopic analysis, in particular, two-dimensional NMR (^1H - ^1H COSY; ^1H - ^1H NOE; ^1H - ^{13}C COSY, COLOC) data.

Key words: Sinopteridaceae; *Onychium lucidum*; Flavone and flavone glycoside; Methoxycyclopolylols.

Onychium is a small genus with about 10 species belonging to the family Sinopteridaceae. *Onychium*, mainly distributed in eastern Asia, is used in traditional Chinese medicine for enteritis, jaundice, flu and fever and as toxicide (Zhou, 1988). The compounds so far isolated from *Onychium* include flavonoids, indanoids, chalcone and diterpenoids (Xu *et al.*, 1993; Akabori *et al.*, 1980; Sengupta *et al.*, 1976; Hasegawa *et al.*, 1974; Banerji *et al.*, 1974; Ramakrishnan *et al.*, 1974).

The phytochemical study on *Onychium lucidum* has not been reported. The present paper describes the isolation, structural elucidation and identification of these ten constituents from *Onychium lucidum*.

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Results and Discussion

Luteoloside (1) $C_{21}H_{20}O_{11}$ $[M]^+$ 448, has strong IR absorption bands for hydroxyl groups ($3420 - 3100 \text{ cm}^{-1}$) and the characteristic peaks due to the flavonol skeleton ($1646, 1585 \text{ cm}^{-1}$). This was further supported by typical UV absorption at 256, 266, 348 nm (Nomura *et al*, 1978). The ^{13}C NMR data (Table 2) also revealed the presence of a flavone and a glucose unit. Its aglycone was very similar to those of $3', 4', 5, 7$ - tetrahydroxyflavone (luteolin) in the ^{13}C NMR spectra (Wagner *et al*, 1976). Comparison of the ^1H NMR spectra of 1 with that of luteolin showed the presence of δ 6.78 for $3 - \text{H}$ signal and the extreme downfield characteristic δ 12.98 for $5 - \text{OH}$ signal due to the intramolecular hydrogen bonding (Roitman *et al*, 1993). In addition, if glucose unit was attached to $C - 3'$ or $C - 4'$, then the signals of $C - 2'$ and $C - 4'$ or $C - 3'$ and $C - 5'$ would be downfield shifted (Markham *et al*, 1978). Therefore, glucose unit only could be attached to the $7 - \text{hydroxyl group}$. On the basis of the above evidence, we assigned 1 as luteolin - $7 - \text{glucoside}$ (Kokkalou *et al*, 1988), namely $2 - (3, 4 - \text{dihydroxyphenyl}) - 7 - (- \text{D} - \text{glucopyranosyloxy}) - 5 - \text{hydroxy} - 4\text{H} - 1 - \text{Benzopyran} - 4 - \text{one}$.

3, 7 - Dimethylquercetin (2), $C_{17}H_{14}O_7$ $[M]^+$ 330 have strong IR absorption bands for hydroxyl groups ($3390, 3140 \text{ cm}^{-1}$) and the characteristic peaks due to the flavonol skeleton ($1640, 1575 \text{ cm}^{-1}$). This was further supported by typical UV absorption at 256, 296, 356 nm (Nomura *et al*, 1978). The ^{13}C NMR data (Table 2) also revealed the signals of a carbon skeleton of a flavone and two methoxyl groups. The flavonol has very similar ^{13}C NMR data to those of $3, 3', 4', 5, 7$ - pentahydroxyflavone (quercetin) (Wagner *et al*, 1976). The locations attached of two methoxyl groups were deduced as follows. Comparison of the ^1H NMR spectra of 2 with that of quercetin was showed that the two hydroxyl groups at the $C - 3$ and $C - 7$ in quercetin had replaced, the two methoxyl groups at $C - 3$ and $C - 7$ in 2, according to the lack $7 - \text{OH}$ (ca. δ 9.5) and $3 - \text{OH}$ (ca. δ 10.6) signals and the presence of 12.68 for $5 - \text{OH}$ signal due to the intramolecular hydrogen bonding in 2 (Roitman *et al*, 1993). In addition, the downfield shift of the $C - 2$ and $C - 4$ signals from δ 146.9 and 175.9 in quercetin to δ 155.91 and 177.95 in 2 and the upfield shift of the $C - 6$ and $C - 8$ signals from δ 98.3 and 93.5 in quercetin to δ 97.62 and 92.13 in 2 also were confirmed that the two methoxyl groups were attached the $C - 3$ and $C - 7$ position in 2, respectively. Therefore, the structure of 2 was assigned as 3, 7 - dimethylquercetin, namely $2 - (3, 4 - \text{dihydroxyphenyl}) - 3, 7 - \text{dimethoxyl} - 5 - \text{hydroxy} - 4\text{H} - 1 - \text{Benzopyran} - 4 - \text{one}$.

Contigoside B (3), $C_{21}H_{20}O_{12}$, $[M]^+$ 464. The ^{13}C NMR data revealed the presence of a flavone and a glucose unit. Its aglycone unit was very similar to those of $3, 3', 4', 5, 7$ - pentahydroxyflavone (quercetin) in ^{13}C NMR data (Wagner *et al*, 1976). Comparison of the ^1H NMR spectra of 3 with that of quercetin showed the lack of the extreme downfield characteristic signal for $3 - \text{OH}$ (~ 10.6) due to the intramolecular hydrogen bonding (Roitman *et al*, 1993). Therefore, this glucose unit could be suggested to the $3 - \text{hydroxyl group}$. This conclusion was supported by ^{13}C NMR data which showed the two the downfield shift of the $C - 2$ and $C - 4$ signals from δ 146.9 and 175.9

in quercetin to δ 156.13 and 177.37 in **3** (Markham *et al*, 1978). On the basis of the above evidence, **3** was determined as quercetin-3-glucoside (Xu *et al*, 1999).

Onychin (4), $C_{27}H_{32}O_{13}$, M 564. The ^{13}C NMR data revealed the presence of a flavanone and a disaccharide moiety. Its aglycone unit has almost the same ^{13}C NMR data to those of 5, 7-dihydroxyflavanone (pinocembrin) (Wagner *et al*, 1976). The disaccharide unit also has almost the same ^{13}C NMR data to those of a β -D-glucopyranose \rightarrow α -L-rhamnoside unit (Markham *et al*, 1978). In addition, the extreme downfield δ 12.46 signal could be assigned to 5-OH due to the intramolecular hydrogen bonding. Therefore, disaccharide unit is attached to the 7-hydroxyl groups. This conclusion was supported by ^{13}C NMR data which showed the downfield shift of the C-6, C-8 and C-10 signals from δ 96.1, 95.1 and 101.9 in pinocembrin to δ 97.85, 96.23 and 104.35 in **4** (Wagner *et al*, 1976). In addition, this conclusion was further confirmed by the detailed 1H - 1H COSY, 1H - ^{13}C COSY and COLOC analyse. So, we assigned **4** as onychin (Xu *et al*, 1993).

Lucidol (5), $C_7H_{14}O_6$, $[M]^+$ 194, was found to have five secondary hydroxyl groups and a secondary methoxy group on the following spectroscopic data: IR $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3390-3150, ^{13}C NMR: δ 87.44 (1C, d), 74.32 (2C, d), 74.01 (2C, d), 73.88 (1C, d), 60.76 (1C, q, OMe); 1H NMR: δ 4.76 (1H, t, J =2.8Hz), 4.67 (2H, t, J =9.4Hz), 4.09 (2H, dd, J =9.4, 2.8Hz), 3.96 (3H, s, MeO), 3.58 (1H, t, J =9.4Hz); The above data suggested that **5** has a cyclohexane nucleus as a basic skeleton. The position of six oxygen functional groups were deduced as follows. The signal at δ 4.76 indicated the existence of methoxy group in axial orientation. The symmetrical signals at δ 4.67 and 4.09 indicated that the four hydroxyl groups are possessed symmetrically in equatorial orientations. The signal at δ 3.58 indicated that the last hydroxyl group also is in equatorial orientation. Thus, the chemical structure of **5** could be represented as 1β -methoxy- 2β , 3α , 4β , 5α , 6β -pentahydroxycyclohexane.

Onychiol B (6), $C_{20}H_{32}O_3$ $[M]^+$ 320, showed the presence of three methyl groups, six methylene groups, five methine groups, two quaternary carbons, and four olefinic carbons in the ^{13}C NMR spectrum. So, **6** would have a three-cyclic skeleton. The IR absorption bands were revealed the presence of hydroxyl groups (3280, 3220, 3100 cm^{-1}) and double bonds (1645, 980, 963 cm^{-1}). The extreme upfield 7.87 ppm signal for 5a-Me due to the intramolecular shielding effect of two adjacent hydroxyl is characteristic of onychiol B. The data of MS, 1H and ^{13}C NMR of **6** were in good agreement with those of onychiol B reported previously (Hseu *et al*, 1980), suggesting that compound **6** was onychiol B.

Experimental

General Kofler melting points were uncorrected; IR were recorded on KBr discs with a Perkin-Elmer 577 spectrometer. UV was obtained in EtOH on a UV-210A spectrometer. EIMS (positive) were measured on a VG Auto Spec-3000 spectrometer with direct inlet 70 or 20 eV. NMR were run on a Bruker AM-400 spectrometer using TMS as internal standard; chemical shift values

are reported in δ (ppm) units (pyridine - d_5 and $CDCl_3$). Coupling constants (J) were expressed in Hz.

Plant material The aerial parts of *Onychium lucidum* were collected in Shiyang, Dayau County, Yunnan, China in August, 1989, and were identified by Prof. S. K. Wu, a botanist of Our Institute. A voucher specimen was deposited in the Herbarium of Kunming Institute of Botany, Academia Sinica.

Extraction and isolation 2 kg dried and powdered of *Onychium lucidum* were extracted with MeOH three times at room temperature for a week, after removal the solvent in vacuum, the residue was subjected on Si gel column chromatography and eluted with gradient $CHCl_3 - CH_3COCH_3$ and $CHCl_3 - MeOH$ system. Ten compounds, luteoloside (1) (14 mg, 0.0007%), 3, 7 - dimethoxy- quercetin (2) (10 mg, 0.0005%), contigoside B (3) (11 mg, 0.0006%), onychin (4) (2.2 g, 0.11%), and 1β - methoxy - 2β , 3α , 4β , 5α , 6β - pentahydroxycyclohexane (5) (16 mg, 0.0008%), onychiol B (6) (15 mg, 0.0008%), β - sitosterol (7), daucosterol (8), oleanolic acid (9) and sucrose (10), were obtained (See Figure 1). Some components were further purified by recrystallization and prep. TCL (silica gel).

Luteoloside (1), $C_{21}H_{20}O_{11}$ M 448, yellow needle crystals (MeOH), mp. $259 \sim 261^\circ C$; $UV\lambda_{max}^{EtOH}$ (log ϵ): 256, 266, 348 nm; $IR\nu_{max}^{KBr}$ cm^{-1} : 3420 \sim 3100, 1646, 1585, 1485, 1436, 1365, 1330, 1253, 1167, 1075, 1020, 850, 832, 775, 740, 620; EIMS 70eV m/z (%): 286 (M - Glc, 80), 258 (8), 229 (5), 153 (20), 144 (4), 134 (13), 124 (9), 115 (3), 105 (25), 91 (10), 73 (35), 60 (100); 1H NMR (DMSO - d_6 , ppm) δ : See Table 1; ^{13}C NMR (DMSO - d_6 ,) δ : See Table 2.

3, 7 - Dimethylquercetin (2), $C_{17}H_{14}O_7$ M 330, yellow needle crystals (MeOH), mp. $232 \sim 234^\circ C$; $UV\lambda_{max}^{EtOH}$ (log ϵ): 256, 296, 356 nm; $IR\nu_{max}^{KBr}$ cm^{-1} : 3390, 3140, 1640, 1575, 1480, 1416, 1360, 1332, 1300, 1225, 1200, 1150, 1115, 1010, 908, 815; EIMS 70eV m/z (%): 330 (M $^+$, 100), 312 (20), 301 (11), 287 (39), 271 (4), 257 (5), 244 (6), 203 (8), 167 (17), 151 (15), 137 (27), 122 (13), 109 (B - ring, 15), 95 (17), 81 (12), 69 (20), 55 (27); 1H NMR (DMSO - d_6) δ : See Table 1; ^{13}C NMR (DMSO - d_6 ,) δ : See Table 2.

Contigoside B (3), $C_{21}H_{20}O_{12}$ M 464, yellow needle crystals (MeOH), mp. $206 \sim 208^\circ C$; $UV\lambda_{max}^{EtOH}$ (log ϵ): 258, 366 nm; $IR\nu_{max}^{KBr}$ cm^{-1} : 3300, 1645, 1595, 1555, 1490, 1432, 1340, 1290, 1260, 1190, 1160, 1105, 1050, 1003, 925, 875, 805; EIMS 70eV m/z (%): 302 (M - 162, 100), 286 (2), 273 (3), 229 (1), 200 (1), 153 (7), 137 (12), 123 (8), 109 (B - ring, 4), 105 (34), 91 (8), 83 (47), 77 (26), 69 (32), 60 (65), 55 (82); 1H NMR (DMSO - d_6) δ : See Table 1; ^{13}C NMR (DMSO - d_6) δ : See Table 2.

Onychin (4), $C_{27}H_{32}O_{13}$ M 564, white needle crystals (MeOH), mp. $279 \sim 280^\circ C$; $[\alpha]^{24.5^\circ} - 112.93^\circ$ (MeOH, C 0.29), $UV\lambda_{max}^{EtOH}$ (log ϵ): 213 (4.46), 286 (4.26), 330 (3.50) nm; $IR\nu_{max}^{KBr}$ cm^{-1} : 3420, 3360, 1655, 1647, 1632, 1574, 1500, 1450, 1394, 1342, 1330, 1322, 1294, 1278, 1226, 1180, 1157, 1085, 1050, 1032, 1015, 994, 978, 885, 844, 820, 775, 750; EIMS

70eV m/z (%): 564 (M⁺, 0.8), 447 (0.4), 418 (M - Rha -, 0.4), 400 (M - Rhamnose, 0.1), 368 (0.8), 354 (0.4), 256 (M - Rha - Glc -, 100), 238 (5), 179 (256 - B - ring, 33), 153 (14), 152 (25), 129 (14), 104 (19), 85 (28), 77 (B - ring, 15), 71 (35), 55 (37); ¹H NMR (C₅D₅N) δ: See Table 1; ¹³C NMR (C₅D₅N) δ: See Table 2; ¹³C - ¹H COSY and COLOC spectra See Table 3.

Lucidol (1β - methoxy - 2β, 3α, 4β, 5α, 6β - pentahydroxycyclohexane) (5), C₇H₁₄O₆ M 194, white amorphous crystals (MeOH), IR_{max}^{KBr} cm⁻¹: 3390 - 3150, 2900, 2880, 2800, 1430, 1395, 1360, 1320, 1295, 1280, 1255, 1240, 1180, 1120, 1100, 1060, 1045, 1015, 930, 920, 875, 745, 710, 605, 465, 420, 360, 300; FABMS m/z (%): 193 (M - 1, 100), EIMS 70eV m/z (%): 195 (M + 1, 24), 177 (M - OH, 7), 162 (M - OH - CH₃, 6), 144 (M - OH - CH₃ - H₂O, 42), 127 (M - 2OH - CH₃ - H₂O, 13), 116 (47), 103 (40), 87 (94), 73 (100), 60 (74); ¹H NMR (C₅D₅N) δ: 4.76 (1H, t, J = 2.8Hz, 1α - H), 4.67 (2H, t, J = 9.4Hz, 3β, 5β - H), 4.09 (2H, dd, J = 9.4, 2.8Hz, 2α, 6α - H), 3.96 (3H, s, MeO), 3.58 (1H, t, J = 9.4Hz, 4α - H); ¹³C NMR (C₅D₅N) δ: 87.44 (d, C - 1), 74.32 (d, C - 2), 74.01 (d, C - 3), 73.88 (d, C - 4), 74.01 (d, C - 5), 74.32 (d, C - 6), 60.76 (q, OMe).

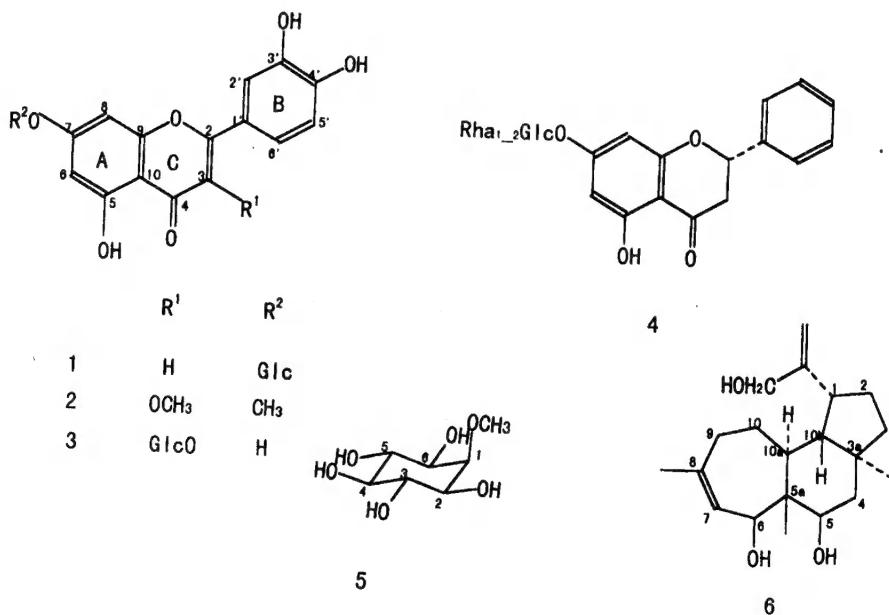


Fig. 1 Chemical Constituents of *Onychium lucidum*

Onychiol B (6), C₂₀H₃₂O₃ M 320, white cubic crystals (MeOH), mp. 209 ~ 210°C; IR_{max}^{KBr} cm⁻¹: 3280, 3220, 3100, 1645, 1468, 1445, 1380, 1354, 1308, 1180, 1154, 1068, 1035, 1026, 1000, 980, 963, 933, 903; EIMS 70eV m/z (%): 320 (M⁺, 3), 305 (0.5), 287 (2), 269 (1), 201 (7), 185 (20), 175 (11), 159 (18), 145 (22), 133 (20), 119 (40), 105 (37), 91 (51), 84 (54), 79 (45), 67 (30), 55 (70), 41 (100); ¹H NMR (C₅D₅N) δ: 7.85,

6.64, 5.19 (each 1H, br s, $3 \times$ OH), 5.75 (1H, br s, 7-H), 5.50, 5.11 (each 1H, br s, C = CH₂), 4.86 (1H, br s, 6 α -H), 4.48 (1H, dd, 11.6, 3.9, 5 α -H), 4.33, 4.28 (each 1H, ABd, 14.6, -CH₂-OH), 2.70 (1H, m, 1 β -H), 1.73 (3H, s, 8-Me), 1.25 (3H, s, 3 α -Me), 1.15 (3H, s, 5 α -Me); ¹³C NMR (C₅D₅N) δ : 51.43 (d, 1-C), 30.95 (t, 2-C), 34.48 (t, 3-C), 41.45 (s, 3 α -C), 46.09 (t, 4-C), 74.81 (d, 5-C), 45.75 (s, 5 α -C), 82.00 (d, 6-C), 133.07 (d, 7-C), 136.25 (s, 8-C), 41.94 (t, 9-C), 24.33 (t, 10-C), 40.30 (d, 10 α -C), 44.61 (d, 10 β -C), 155.40 (s, >C=CH₂), 106.71 (t, >C=CH₂), 66.32 (t, -CH₂OH), 25.66 (q, 8-Me), 22.44 (q, 3 α -Me), 7.87 (q, 5 α -Me).

Table 1 ¹H NMR spectra data of compound (1), (2), (3) and (4) in DMSO-d₆

Hydrogen	1	2	3	4*
H-3	6.78 br s			
H-6	6.74 d, 1.6	6.69 d, 2.0	6.39 d, 1.6	6.73 d, 1.6
H-8	6.43 d, 1.6	6.35 d, 2.0	6.19 d, 1.6	6.67 d, 1.6
H-2'	7.45 d, 2.4	7.58 d, 2.0	7.58 d, 2.4	7.55 d, 7.6
H-3'				7.41 t, 7.6
H-4'				7.36 t, 7.6
H-5'	6.89 d, 7.8	6.90 d, 8.4	6.83 d, 7.8	7.41 t, 7.6
H-6'	7.43 dd, 7.8, 2.4	7.47 dd, 8.4, 2.0	7.57 dd, 7.8, 2.4	7.55 d, 7.6
5-OH	12.98 s	12.68 s	12.63 s	12.46 s
H-2 β				5.40 dd, 12.8, 2.8
H-3 α				3.20 dd, 17.2, 12.8
H-3 β				2.89 dd, 17.2, 2.8
Glc-1-H	5.07 d, 7.2		5.45 d, 7.6	5.70 d, 7.6
Glc-H ₆	3.71-3.17 (6H)		3.58-3.07 (6H)	
3-OMe		3.85 s		
7-OMe		3.78 s		
Rha-1-H				6.38 s
Rha-H ₄				
Rha-Me				1.78 d, 6.0

* In C₅D₅NTable 2 ¹³C NMR spectra data of compound (1), (2), (3) and (4) in DMSO-d₆

Carbon	1	2	3	4*
2	164.40 s	155.91 s	156.31 s	79.40 d
3	103.09 d	137.82 s	133.32 s	43.35 t
4	181.76 s	177.95 s	177.38 s	196.52 s
5	161.05 s	160.88 s	161.18 s	164.43 s
6	99.49 d	97.62 d	98.60 d	97.85 d
7	162.88 s	165.04 s	164.12 s	166.22 s
8	94.68 d	92.13 d	93.43 d	96.23 d
9	156.85 s	156.19 s	156.27 s	163.32 s
10	105.28 s	105.10 s	103.90 s	104.35 s
1'	121.32 s	120.57 s	121.13 s	139.24 s
2'	113.49 d	115.49 d	115.15 d	126.75 d
3'	145.69 s	145.18 s	144.73 s	129.07 d

续表 2

Carbon	1	2	3	4 *
4'	149.84 s	148.75 s	148.39 s	128.98 d
5'	115.91 d	115.64 d	116.16 d	129.07 d
6'	119.06 d	120.57 d	121.51 d	126.75 d
Glucose				
1	99.92 d		100.94 d	99.40 d
2	73.06 d		74.05 d	77.80 d
3	77.10 d		77.44 d	79.07 d
4	69.56 d		69.92 d	74.01 d
5	76.34 d		76.48 d	78.75 d
6	60.60 t		60.95 t	62.03 t
Rhamnose				
1				102.36 d
2				72.31 d
3				72.68 d
4				71.10 d
5				69.81 d
CH ₃				18.78 q
3 - OCH ₃		59.57 q		
7 - OCH ₃		55.95 q		

* in C₆D₅NTable 3 ¹³C-¹H COSY and COLOC spectra of onychin (4) in C₆D₅N

Assignment	¹ H NMR	¹³ C NMR	COLOC observed
H - 2β	5.40 dd, 12.8, 2.8	79.40 d	C - 4, C - 2
H - 3α	3.20 dd, 17.2, 12.8	43.35 t	C - 4,
H - 3β	2.89 dd, 17.2, 2.8		
H - 6	6.73 d, 1.6	97.85 d	C - 5, C - 7, C - 8, C - 10
H - 8	6.67 d, 1.6	96.23 d	C - 7, C - 9, C - 10
H - 2', 6'	7.55 d, 7.6	126.75 d	
H - 3', 5'	7.41 t, 7.6	129.07 d	
H - 4'	7.36 t, 7.6	128.98 d	
Glc - 1 - H	5.69 d, 7.6	99.40 d	
- 2 - H	4.50 dd, 9.2, 7.6	77.80 d	
- 3 - H	4.38 t, 9.2	79.07 d	
- 4 - H	4.35 t, 9.2	74.01 d	
- 5 - H	4.04 ddd, 9.2, 4.8, 2.4	78.75 d	
- 6 - H _a	4.42 dd, 12.0, 2.4	62.03 t	
- 6 - H _b	4.33 dd, 12.0, 4.8		
Rha - 1 - H	6.38 s,	102.36 d	Glc - 2 - C, Rha - 3, 5 - C
- 2 - H	4.79 br s	72.31 d	
- 3 - H	4.54 dd, 9.6, 2.8	72.68 d	
- 4 - H	4.26 t, 9.6	71.10 d	
- 5 - H	4.76 dq, 9.6, 6.0	69.81 d	
- 6 - Me	1.78 d, 6.0	18.78 q	

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